FT-I.R. STUDY OF OXYGENATED FUNCTIONAL GROUPS DISTRIBUTION DURING DRY-PHASE OXIDATION OF COALS.

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INTRODUCTION

When coal is oxidized with air in dry-phase conditions at temperatures higher than 150 °C, besides the well known alteration of several coal properties [1], a mixture of base extractable substances is formed in considerable yields after a few hours [2]. These substances are generally referred to as regenerated humic acids (RHA). Although details of chemical changes in coal "molecule" caused by air oxidation are only partially understood, the results of spectroscopic and chemical studies on dry oxidized coals are consistent with a preferential oxidation of the aliphatic part of coal structure, leading to a more aromatic product and to a concomitant formation of various oxygenated functional groups (-COOH, C=O, CO-O-CO, etc.)[3,4]. In a previous FT-ir study [4], performed on a subbituminous B coal oxidized between 175 and 275 °C, only the overall trend of carbonyl groups was presented and no considerations about the behavior of hydroxyl groups were made owing to the complexity of regions where oxygenated functional groups absorb The objective of this work was to detect and determine, the formation and relative changes in concentration of various oxygenated functional groups as a function of oxidation time by applying the curve-resolving procedure and acetylation of coal samples. The aim was to gain a better understanding of the structural modification which occur during the formation of RHA.

EXPERIMENTAL

Two U.S coals (M. Rosebud and a subbituminous B) were used in this study. Their ultimate and proximate analyses are given in table 1. The as received coals were crushed, sieved and the fraction 106-250 μm was used throughout this investigation. Oxidation tests were performed in a steel fluid bed reactor, at 200 °C, with air pressure of 0.2 MPa and reaction times up to 4 hours. For each run the reactor was charged with 30 g of dried coal heated (in flowing N_2) and pressurized. Subsequently the coal sample was reacted switching over the nitrogen flow with a controlled flowrate of preheated air. For all runs the gas superficial velocity was 5.1 cm/sec. After reaction, oxidation was stopped by feeding nitrogen and after that the reactor was depressurized and cooled to room temperature. Finally, the oxidized coal samples were subjected to elemental analysis, characterized by FT-ir spectroscopy and selected samples were acetylated to determine hydroxyl groups. Experimental procedures used for preparing KBr pellets and obtaining FT-ir spectra of coal samples have been described elsewhere [4].The latter were obtained on a Digilab FTS/15 FT-ir spectrometer. The

characterization of region between 1900 and 1450 cm^{-1}, was achieved through curve-fitting procedure, performed using the software supplied with the Data General processing system. The parameters requested in deconvolution procedure are mainly the number of bands, their positions, the gaussian coefficient and the base line intercepts. The gaussian coefficient was fixed at 0.3. The number of bands was determined after a critical examination of the second derivative of the spectra. Their position was recalculated iterating the fitting procedure. For each spectrum the base line was drawn between two points where no absorption occurs, namely around 1800 and 730 cm^{-1}. Acetylation of raw and oxidized coal samples was conducted following the procedure set up by Blom et al.[5]. No attempt was made to demineralize the coal samples prior acetylation.

RESULTS AND DISCUSSION

Figure 1 shows FT-ir spectra of Montana Rosebud coal at various oxidation degrees. From a general point of view the evolution is similar for both coals and as observed by other investigators [6] the most remarkable changes are those occurring in the regions 3000-2700 cm^{-1} (aliphatic C-H_1 stretching), 1800-1600 cm^{-1} (C=O stretching) and 1300-1000 cm^{-1} (-C-O-C- stretching, phenolic and alcoholic C-O stretching, OH bending, etc.). As the reaction time increases the absorption due to aliphatic groups decreases while the absorption bands due to C=O stretching and present in the region 1300-1000 cm^{-1} display a noteworthy increase. Figure 2 shows the FT-ir spectrum of subbituminous B coal between 1870 and 1450 cm^{-1} and its second derivative. Upon examination, fig.2 reveals the presence of three well defined maxima (1770, 1718 and 1608 cm^{-1}) and shoulders or secondary maxima to be distinguished from possible artifacts. This situation was verified to be valid for each spectrum of coal samples examined. As an example of the results obtained through curve fitting procedure, fig. 3 shows the infrared spectrum of a oxidized coal sample curve-resolved into nine bands. The choice of number and position of component bands was made on the basis of the second derivative of spectrum, FT-ir measurements on ion exchanged and acetylated coal samples and results obtained by other investigators in similar works [7,8,9]. Assignments of component bands are given in table 2. In this connection it is important to stress that owing to unavoidable interference of adjoining bands, the presence of different molecular situations and its modifications caused by oxidation, the absorption frequency of bands resulting from the curve fitting procedure have undergone slight shifts (generally ± 5 cm^{-1}) during reaction. The structural changes observed were similar for both coals examined and the most remarkable concerned the bands at 1771, 1734, 1711, 1684 and 1648 cm^{-1} whose evolution is reported in figures 4 and 5. On the contrary bands located at 1608, 1585, 1568 and 1542 cm^{-1} as expected did not display significant variations. The results presented in the figures 4 and 5 show that the evolution of different functional group containing C=O is qualitatively similar for both coals and as the reaction proceeds the concentration of each group increases. However significant differences exist between the two coals as regards the formation rates and relative concentration of various C=O groups during reaction.
Previous results obtained by FT-ir and ^{13}C-NMR [4,10] showed that at 200 °C the oxidation occurs almost exclusively on the aliphatic part

of coal structure. Therefore the formation of different oxygenated
functional groups detected by I.R. spectroscopy can be explained in
terms of oxidative destruction of aliphatic structures. Considering
the Wiser model of coal structure [11], where polyaromatic and
hydroaromatic units are joined by short aliphatic chains and various
ether linkages to form a three-dimensional network, it is possible
to single out some structural units, which through the oxidation of
aliphatic part, can give rise to the formation of detected
oxygenated functional groups. Some possible reaction pathways,
worked out on the basis of the results obtained, and considering the
different reactivity of various structures towards the oxygen , are
given in figure 6. The changes in hydroxyl groups content (alcoholic
and phenolic) upon oxidation at 200 °C was determined by measuring
the area of the peaks centred at 1367 cm^{-1} (CH$_2$ bending) and 1187
cm^{-1} (-C-O- stretching) of acetylated coal samples. Before
discussing the data it is important to stress that the bands used to
follow the hydroxyl behavior are due to phenolic and alcoholic
group. However literature data[9] show that the content of the
latter is much lower than that of phenolic group. In addition, some
results of curve fitting procedure of the complex spectral band due
to the C=O stretching of acetyl group indicate that the R-OH/Ar-OH
ratio remains almost constant during reaction at 200 °C. Therefore
the trend observed should reflect the behavior of phenolic group.
The trend reported in figure 7 shows a noteworthy decrease of
hydroxyl groups contents in the first hour of oxidation followed by
a levelling off at longer reaction times. It is known that the
presence of hydroxyl groups activate the aromatic ring towards
oxidation and that phenols are easily oxidized to quinones, which
subsequently can evolve to carboxyl through rupture of benzenic ring
[12]. Therefore the observed trend can be interpreted by the
reaction scheme given below:

1660 - 1690 cm-1
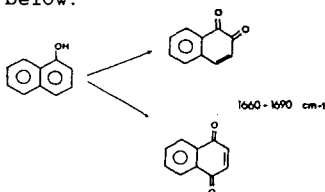
Furthermore, the disappearance of hydroxyl groups can also be a
result of condensation reactions between hydroxyl and carboxyl or
hydroxyl groups to form esters and ethers bonds respectively. The
latters might have a negative effect on RHA formation for the
alkaline hydrolysis of ether bond occurs with difficulty and demands
more drastic conditions than those used to determine the alkali
solubility of oxidized coal [2,13].

CONCLUSIONS

The changes of coal structure caused by molecular oxygen at 200 °C
have been evaluated by FT-ir spectroscopy and acetylation of coal
samples. The results indicate that the oxidative process leads to
the formation of different oxygenated functional groups such as
carboxyls, ketones, conjugated carbonyls and various type of esters.
Their evolution with time as well as the trend of hydroxyl groups

has been determined. On these grounds some reaction pathways which explain the oxygenated functional group formation in terms of oxidative attack of aliphatic structure have been presented. Keeping in mind the coal structure proposed by Wiser [11], a major conclusion of this work is that formation of RHA should be mainly associated with the break-down of aliphatic structure which lead to smaller fragments (through oxidation of links between aromatic and hydroaromatic clusters) and to a concomitant increase of oxygenated functional groups which make these substances soluble in alkali solution.

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	Sub.B[*]	M. Rosebud[*]
%C	63.5	63.0
%H	4.7	4.1
%N	1.1	1.0
%S	0.9	0.7
%O (by diff.)	20.5	14.7
%Ash	9.6	16.5
%V.M.	44.1	39.4

* moisture free basis

Table 1. Characteristics of utilized coals

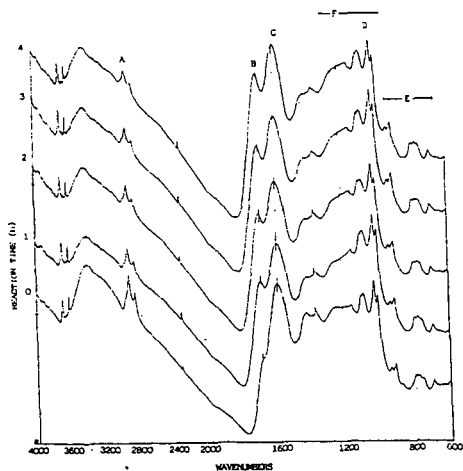| Wavenumber (cm^{-1})	Assignment
1770	Ar-O-CO-R (1775-1765)
1734	R-O-CO-R (1750-1735)
	Ar-CO-OR; Ar-O-CO-Ar (1740-1715)
1711	-COOH (1720-1705)
1684	Ar-CO-R (1700-1670)
1648	Ar-CO-Ar (1680-1640)
	Quinones as: 2 C=O in two rings (1655-1635)
1608	aromatic stretching
1585	aromatic band [9]
1562	$-COO^-M^+$
1541	$-COO^-M^+$

Table 2. Band Assignments

Figure 1. FT-ir spectra of Montana Rosebud coal at various oxidation degrees. A: aliphatic; B: C=O stretching; C: aromatic stretching; D: mineral matter; E: aromatic C-H out of plane bending; F: C-O stretch., C-C stretch., OH bending, etc.
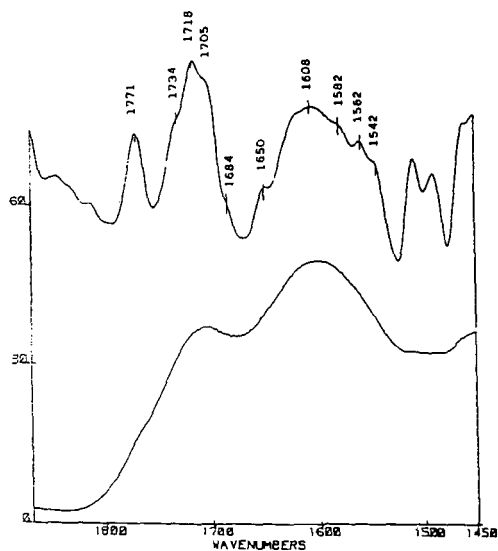
734

Figure 2. Bottom : FT-ir spectrum of oxidized subbituminous B
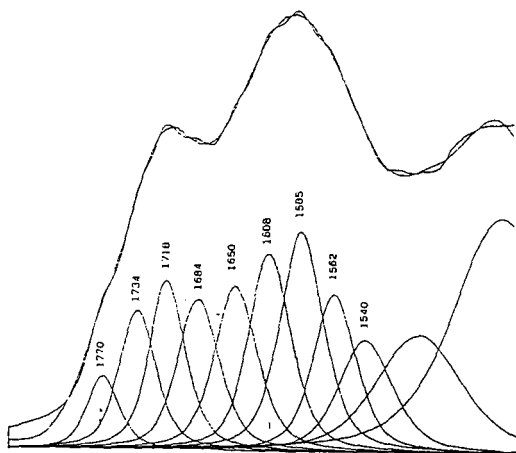coal between 1850 and 1450 cm^{-1}
Top: Second derivative of spectrum

Figure 3. FT-ir spectrum of oxidized Montana Rosebud coal
between 1850 and 1450 cm^{-1} and component bands
from curve fitting procedure.

area (arbritary units)

Figure 4. M. Rosebud coal,
evolution of various
oxygenated functional
groups containing C=O

1200

1000

800

600

400

200

0

0   1   2   3   4   5

time (h)

• 1771   + 1734   * 1711   □ 1682

area (arbritary units)

1400

1200

1000

800

600

400

200

0

0   1   2   3   4   5

time (h)
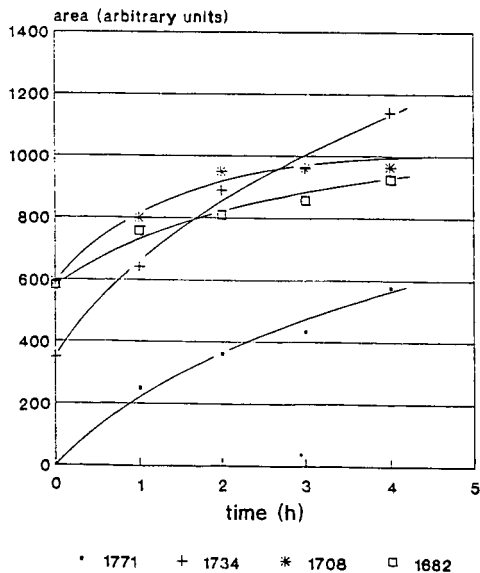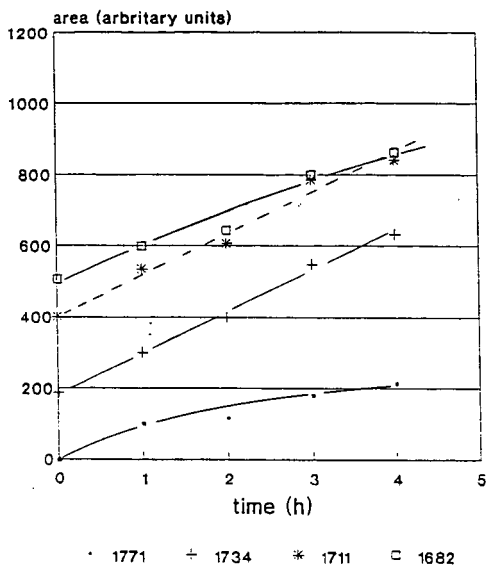
Figure 5. Subbituminous B
coal, evolution of various
oxygenated functional
groups containing C=O

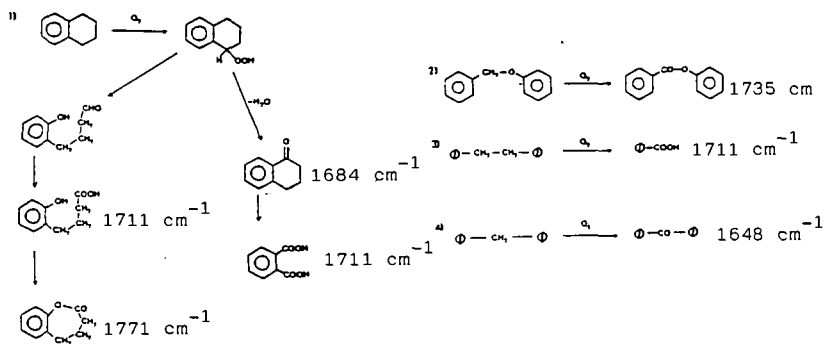• 1771   + 1734   * 1708   □ 1682

736

Figure 6. Scheme depicting the proposed reaction pathways that
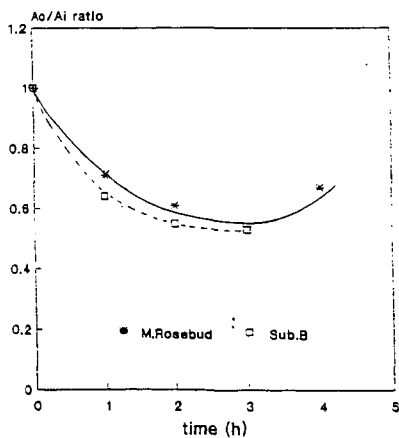may occur during the oxidation on the grounds
of FT-ir results.

Figure 7. Graph of the
fractional change in the
peak area (1187 cm^{-1}) of
of hydroxyl groups versus
oxidation time.